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RELATIONSHIP OF SURFACE AREA OF pH-DEPENDENT SUSPENSIONS AND WATER RETENTION

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ABSTRACT

The equilibrium water retention, M_w/M_s, of suspensions having a pH-dependent surface charge (carbonate-containing aluminum hydroxide and fumed silica) appears to be due to water adsorbed by the surface as well as water retained in pores. The water retained in pores has a lower limit determined by the closest packing porosity. Maximal water retention occurred when the pH was equal to the point of zero charge and attractive particle interactions predominated. The contribution of pore water to M_w/M_s can be minimized by selecting a pH significantly different from the point of zero charge. The water retention properties of the suspension under these conditions are believed to be due to adsorption and the closest packing porosity. Preliminary results indicate that this M_w/M_s can be related to the surface area of the suspended solid.

INTRODUCTION

A recent study of water retention by slurries of 35 different sodium saturated montmorillonites indicated that the specific surface area was directly related to the water content at equilibrium[1]. This observation suggests that the surface area of suspended solids may be determined without drying the suspensions. This would be very desirable for pharmaceuticals as bioavailability and drug action are likely to be more closely related to the surface area in contact with the liquid phase than the surface area of the dry drug. Newman[2] has also suggested that measurement of water adsorption by moist soils under controlled conditions can be used to measure the total specific surface for soils classed as smectitic and having a large cation exchange capacity. These studies[1,2] have dealt mainly with clays which have a fixed surface charge, whereas, most drugs exhibit a pH-dependent surface charge. Therefore, a study was undertaken to determine if the water retention properties of dispersed solids having a pH-dependent surface charge could be related to the surface area in contact with the liquid media.

EXPERIMENTAL

The amorphous carbonate-containing aluminum hydroxide suspension (Chattem Chemical Co., Chattanooga, TN) and the fumed silica (M-5, MS-7, MS-75, HS-5, Cabot Corporation, Boston, MA) were obtained commercially. The amorphous carbonate-containing aluminum hydroxide suspension was adjusted to the desired pH by the addition of 1 N HCl or 1 N NaOH and each sample was diluted to contain 9.2% equivalent aluminum oxide as determined by chelatometric titration[3]. Five percent w/w suspensions of fumed silica were prepared. Following pH adjustment with either 1 N HCl or 1 N NaOH the fumed silica suspensions were diluted to 4.7% w/w. The point of zero charge was determined by use of a continuous titration procedure[4].

A standard technique to determine water retention by soils[5] was used for this study. A pressure plate cell, 27.5 cm. diameter (Soil Test, Inc., Evanston, IL) was sealed in a pressure chamber having a port for delivering nitrogen gas at the desired pressure and a port for the outflow tube. The pressure plate cell consists of a porous ceramic plate covered underneath with a thin neoprene diaphragm and sealed to the edges to serve as a collection conduit. An internal screen provides a passage for the flow of water. An outlet stem connects this collection conduit to an outflow tube fitting which connects to the atmosphere outside of the pressure chamber. The nitrogen gas line was connected to a manometer to monitor pressure. The outflow tube emptied into a buret to allow measurement of water outflow. The specific procedure was as follows:

1. The pressure plate cell was presoaked in distilled water for at least 24 hours prior to use. Care was taken to avoid submerging the drainage tubing.

2. The suspensions were titrated to the desired pH by an automatic titrator (Radiometer, Copenhagen, Denmark) and diluted to final volume at least 24 hours prior to the start of the experiment to ensure equilibration.

3. Premoistened 0.05 um membrane filters were placed on the porous ceramic plate. Polymethyl methacrylate holding rings (3.1 cm i.d., 1 cm high) which held 8 mL were sealed to the pre-moistened membrane filter with high vacuum grease. Twelve samples could be placed on the porous ceramic plate.

4. The pH of each sample was verified and readjusted, if necessary, before an 8 mL sample was placed in a ring.

5. The pressure chamber was sealed and the desired pressure gradually developed. Slight adjustments were made in the rate of nitrogen flow during the experiment to maintain the desired pressure.

6. Water outflow was monitored until no further water flowed into the collection buret, i.e., the system had equilibrated at the applied pressure. Equilibration typically required about 48 hours.

7. The applied pressure was discontinued as soon as the system equilibrated. The pressure chamber was opened and portions of each sample were quickly transferred to tared vials

which had been previously heated to remove any organic material and immediately weighed. This weight was termed wet weight.

8. Samples were dried at 105°C for 24 hours and then placed in a desiccator to cool. The vials were then weighed to obtain the dry weight.

9. The samples were returned to the 105°C oven until a constant weight was obtained.

10. The mass of water, M_w, per mass of solid, M_s, at equilibrium was calculated by Equation 1.

$$\frac{M_w}{M_s} = \frac{(\text{wet weight} - \text{tare}) - (\text{dry weight} - \text{tare})}{(\text{dry weight} - \text{tare})} \qquad \text{Eq.}$$

RESULTS AND DISCUSSION

The precision of the equilibrium water retention method was studied by running 3 identical samples of an amorphous carbonate-containing aluminum hydroxide on 3 different occasions at a pressure of 1 atmosphere. The standard deviation was 1.54%.

The equilibrium water content expressed as mass of water per mass of solid, M_w/M_s, of an amorphous carbonate-containing aluminum hydroxide suspension was determined at 1 atmosphere between pH 5.5 and 6.5. As seen in Figure 1, Line A, the equilibrium water content varied by approximately 50% over the pH range. However, a systematic increase in M_w/M_s was observed as the pH increased. The point of zero charge (PZC) of the amorphous carbonate-containing aluminum hydroxide was 6.9.

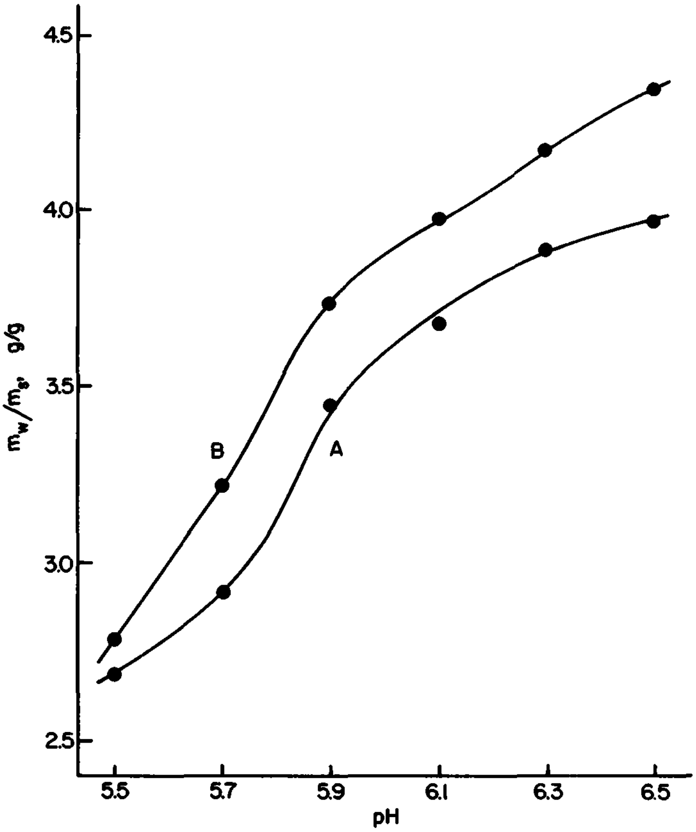

FIGURE 1

Effect of pH on the equilibrium water content, M_w/M_s, of an amorphous carbonate-containing aluminum hydroxide suspension at 1.0 atmosphere, A, and 0.25 atmospheres, B. The 0.25 atmosphere data points represent the average of duplicate samples.

Because the pH range studied was below the PZC, all samples had a positive surface charge, but the surface potential decreased as the pH approached 6.9. The significant increase in M_w/M_s observed with decreasing surface potential would not occur if adsorption of water to the solid's surface was the sole mechanism of water retention. Therefore, mechanism(s) in addition to adsorption must be contributing to water retention by the amorphous carbonate-containing aluminum hydroxide.

At pH conditions near the PZC where the surface charge approaches zero, the theory of Derjaguin, Landau, Verwey and Overbeek (DLVO theory) predicts that particle interactions will be chiefly influenced by attractive van der Waals forces[4,6]. Therefore, attractive particle interactions are expected to increase as the pH increases from 5.5 to 6.5. Attractive particle interactions can lead to a 3-dimensional particle network. As the attractive particle network becomes more extensive, the porosity of the system increases. Increased porosity arising from attractive particle networks will continue to be present in the filter cake after sediment formation, which necessarily occurs during the measurement of water retention. Conversely, at pH conditions away from the PZC the surface charge increases and repulsive electrostatic interparticle forces become important. Under these conditions the process of sediment formation favors a denser, closer packing type of filter cake. When the surface charge is sufficiently great to allow closest packing of the particles in the filter cake, the system should possess the minimum porosity attainable under the applied pressure. The authors have chosen to refer to this as the closest packing porosity. Therefore, it was hypothesized that the pH-dependent water retention by amorphous carbonate-containing aluminum hydroxide seen in Figure 1, Line A, is due to additive mechanisms: water adsorbed by the surface as well as water retained in pores (which has a lower limit determined by the closest packing porosity).

The authors do not intend to infer that adsorbed water and pore water exist as two distinct phases separated by a finite boundary. As the distance from the surface increases, it is likely that the properties of water gradually assume those of bulk water. Also, the mechanism of water adsorption on the surface is not being addressed in the study. Hypotheses to explain the uptake of water by a solid are already in the literature. For example, the swelling pressure of clays has previously been regarded as arising from the osmotic effect of the double layer ions[7]. More recently, it has been hypothesized that water is adsorbed by a nonspecific interaction with the surface[8-10]. The latter hypothesis is favored by the present authors. However, in this study, it is simply desired to view retained water as either being influenced by the surface (adsorbed water) or possessing the properties of bulk water (pore water).

Assuming water is not influenced by the surface throughout the entire void space in the particle packing, a lower limit of pore water will be present in the closest packing porosity. Furthermore, when particle arrangements are formed with increased porosity, more water will be retained due to the increased amount of pore water. Therefore, a quantitative increase in water retention is viewed as the retention of a mass of water in excess of the limiting mass, which is comprised of adsorbed water and pore water present in the closest packing porosity.

The hypothesis of additive mechanisms of water retention was tested by determining the equilibrium water content in the same pH range but at 0.25 atmosphere pressure. As seen in Figure 1, Line B, water retention increased with decreased applied pressure at fixed pH as more water was retained in the samples subjected to 0.25 atmosphere, compared to the corresponding samples subjected to 1.0 atmosphere. In addition, the greatest increase occurred at pH conditions close to the PZC. This behavior is consistent with the hypothesis, as fewer pores in the particle network would be expected to collapse at 0.25 atmosphere applied pressure relative to 1 atmosphere. Therefore, the application of a smaller force leads to less compaction of the sediment and less decrease in porosity during sediment formation. These effects due to lowering the applied pressure are more pronounced as the PZC is approached since more pores are present to be affected.

The water retention-pH profile of amorphous carbonate-containing aluminum hydroxide at pH conditions where dissolution is minimal is presented in Figure 2. Maximum water

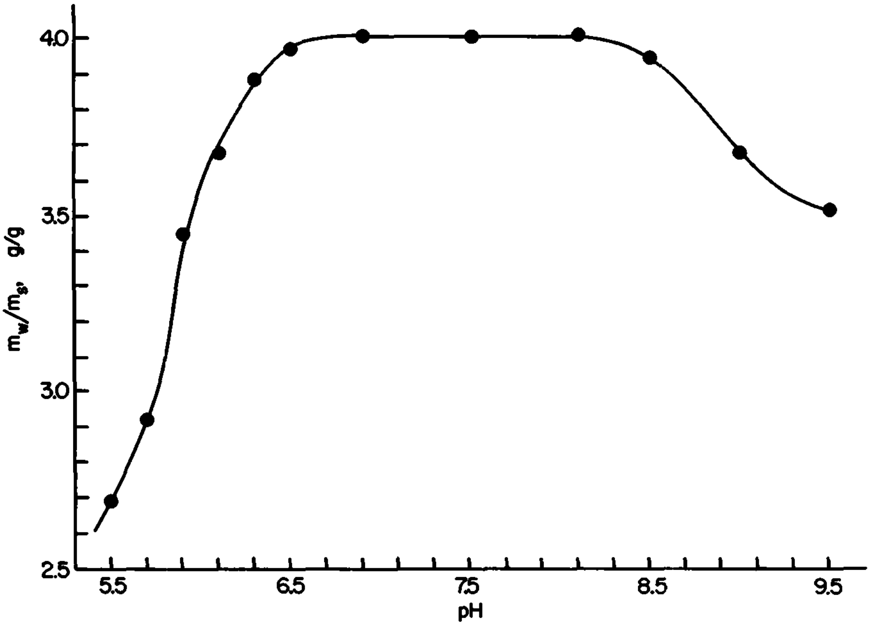

FIGURE 2

Effect of pH on the equilibrium water content, M_w/M_s, of an amorphous carbonate-containing aluminum hydroxide suspension at 1 atmosphere.

retention occurred between pH 6.5 and 8.1. This region includes the PZC (6.9) but the PZC is not at the center of the region of maximum water retention.

The PZC-pH relationship has been found to affect the physical properties of suspensions of solids having a pH-dependent surface charge. The viscosity was maximal[4] and the diffusion coefficient of the particles was minimal[11] when the pH equaled the PZC. This is believed to be due to the increased attractive particle interactions which occur when the surface charge is zero. The water retention behavior seen in Figure 2 follows the same pattern and is also believed to be influenced by the formation of a particle network when the surface charge approaches zero. It is interesting to note that neither the viscosity nor the diffusion coefficient were symmetrical about the PZC. This same asymmetrical behavior was seen in this study in terms of water retention. Thus, the hypothesis that water held in pores formed by attractive particle interactions contributes to the water retention properties of pH-dependent suspensions is supported by Figure 2. It should be noted in moving away from the PZC to both higher and lower pH values that M_w/M_s does not decrease to a constant minimum value. This is interpreted to indicate that pore water arising from attractive particle networks appears to be significant over the entire pH range studied. It appears that water retained in pores is greater than the lower limit contributed by the closest packing porosity in this region.

Fumed silica was selected to further test the hypothesis. Fumed silica was selected because it also has a pH-dependent surface charge. However, its point of zero charge was 3.65, which is substantially different from the amorphous carbonate-containing aluminum hydroxide. The water retention-pH profile for 4.7% w/v fumed silica dispersions is presented in Figure 3. The pH range was limited to pH 2-9 to minimize the dissolution of fumed silica. Water retention was maximal near the PZC and

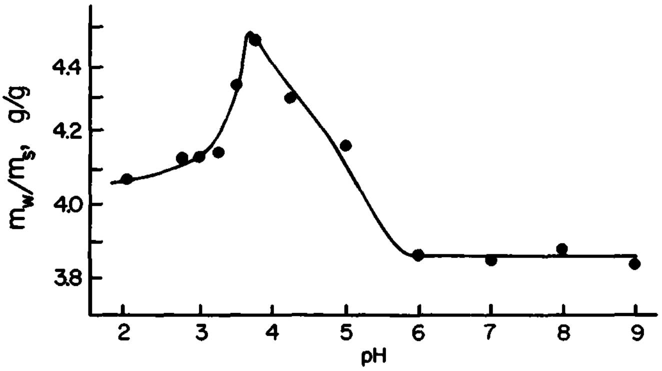

FIGURE 3

Effect of pH on the equilibrium water content, M_w/M_s, of a fumed silica suspension at 1 atmosphere.

decreased to a constant value between pH 6 and 9. The water retention behavior of fumed silica observed can be explained based on the additive contribution of water adsorbed by the surface and water retained in pores by the attractive particle network and the closest packing porosity. Maximal water retention occurred when the pH was near the PZC and attractive particle interactions predominated.

It is interesting that fumed silica exhibited a fairly sharp maximum in M_w/M_s at pH conditions close to the PZC. In contrast, amorphous carbonate-containing aluminum hydroxide had a broad maximum in M_w/M_s which extended over a wide pH range which included the PZC. The fumed silica used in this study is composed of nearly monodisperse 0.014 um spheres while amorphous carbonate-containing aluminum hydroxide is composed of much smaller, polydisperse plate-like particles[12,13]. Since particle interactions are favored in systems of irregular, polydisperse particles, the contrasting behavior observed for the two systems is reasonable when particle interactions are considered. The amorphous carbonate-containing aluminum hydroxide system possesses extensive interparticle interactions except when the PZC-pH is sufficient for repulsive interactions to become significant.

It is important to note that M_w/M_s exhibited a constant, minimum value between pH 6 and 9 for the fumed silica dispersions. In this region, the particles possess a high negative surface charge which prevents attractive particle networks from forming. It is believed the surface charge is sufficient in this range to allow only the closest packing porosity to remain in the filter cake. Therefore, the water retained by the fumed silica between pH 6 and 9 is interpreted to be due only to the adsorption of water and the retention of water by the closest packing porosity. If this value represents the minimal water retention possible under the applied pressure, then the equilibrium M_w/M_s in this pH range most closely corresponds to the M_w/M_s values determined by Low[1] for a series of montmorillonite slurries and should be related to the surface area of the suspended solid.

In order to make a preliminary investigation of the relationship between M_w/M_s and surface area, the water retention by grades of fumed silica having different surface areas was measured at 1 atmosphere and pH 7.0. Specific surface area values were obtained by BET nitrogen adsorption. The BET nitrogen adsorption specific surface area values for fumed silica may not be identical to the surface area in contact with water in the aqueous dispersion; however, if a proportional relationship exists between the two, then M_w/M_s and BET surface area should be correlated. Figure 4 plots the relationship between M_w/M_s and BET surface area for the different grades of fumed silica. The linear correlation between M_w/M_s and BET surface area is high ($R^2 = 0.983$). This indicates that the water retention method has potential for evaluating the surface area of pH-dependent solids in the aqueous suspended state.

A method to determine the surface area of solids dispersed in water would be very valuable for pharmaceutical suspensions. Unfortunately, an accurate measurement of the surface area of a solid dispersed in the original aqueous state is difficult (if not impossible) to obtain. The use of conventional methods requires the dispersed phase to be completely dried. This drying process can lead to significant changes in the particle arrangements, such as aggregation. Also, the drying process can promote crystal growth or polymorphic transformations. Therefore, the surface area as determined by present methods is unlikely to provide an adequate measure of the solid surface in contact with the liquid medium.

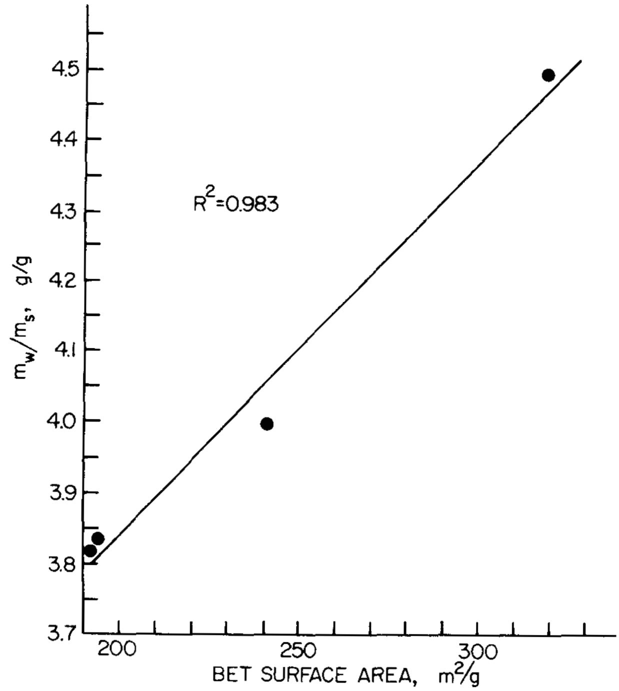

FIGURE 4

Relationship between the equilibrium water content, M_W/M_S, and BET surface area for different grades of fumed silica at 1 atmosphere. All samples were run at pH 7.0.

It is unlikely that a truly absolute surface area could be measured by the water retention method. However, the equilibrium water content may provide an improved indication of the solid surface area in contact with the aqueous phase of a suspension. Under suitable conditions, the amount of retained water should depend primarily upon the solid's "effective" surface area.

In summary, this study investigated the characteristics of retained water in aqueous suspensions of pH-dependent solids. The results provide insight into the factors which must be considered in the future development of this method. It has been shown that water retention varies with pH for solids with a pH-dependent surface charge due to the variable contribution of pore water. Water retention due to pores was shown to be minimized by selecting conditions where the particles are highly charged and attractive particle interactions are not present. It is believed that the water retained under these conditions is due to the adsorption of water by the surface and water held by the closest packing porosity. It was shown that M_W/M_S is directly related to BET surface area for fumed silica dispersions prepared under these conditions.

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